

***RELATIONSHIP OF REFRACTIVE INDEX TO DENSITY AND
MIXING RULES FOR AMBIENT AEROSOLS***

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Abstract

Although refractive index and mass density as two fundamental properties have been extensively investigated, they have been largely treated in a separate and independent way. Here a wealth of data on refractive index and mass density for pure materials (e.g., organics, inorganics and minerals) and inhomogeneous mixtures including aerosols are collected and examined, showing that refractive index and mass density are in fact closely related to each other. Theoretical analysis reveals that a denser material tends to have a larger refraction index because of a greater number of induced electric dipoles when it is exposed to an electric field. An analytical expression that relates refractive index to mass density for pure material is derived, and further extended to inhomogeneous mixtures such as ambient aerosols by formulating a self-consistent effective medium theory. Analysis of the effective medium theory further reveals that the mixing rule for calculating the effective refractive index of aerosol particles should be consistent with the corresponding relationship between refractive index and mass density, providing theoretical guide for choosing the mixing rule to calculate aerosol refractive index.

1. Introduction

Refractive index is a fundamental optical property of aerosol particles that determines light scattering by small aerosol particles (van de Hulst 1957; Bohren and Huffman 1983). Material mass density is a fundamental physical property of aerosol particles that is crucial for studying aerosol dynamics such as deposition (Seinfeld and Pandis 1997). These two quantities are also often required together in many areas of aerosol research. For examples, a variety of instruments that have been developed over the last few decades use different approaches to measure aerosol number size distributions (see McMurry 2000 for a recent review). The instruments built on the principle of aerosol dynamics such as impactors measure the "aerodynamic size" that depends on particle density, in addition to the geometrical size and geometrical shape. The "electric mobility size" obtained by electrostatic classification such as DMA depends on particle shape and size, but not on density. "Optical sizes" by optical spectrometers depend on particle size, shape, as well refractive index. These measures of particle size can be very different, depending on the specific properties involved in the instruments. Converting from one measure of size to another typically requires information on particle refractive index and mass density. Therefore, accurate knowledge of refractive index and density of aerosol particles is critical for comparing measurements built on different principles. Another area that requires both refractive index and density of aerosol particles is quantification of aerosol effects on climate, which calls for coupling of aerosol dynamics models with aerosol optics models.

Despite the simultaneous need for both quantities, refractive index and density have been largely investigated, treated, and used in a separate and independent way by aerosol optics and aerosol dynamics communities. No studies have been devoted to the relationship between these two fundamental aerosol quantities, and as a result, it is unclear if there is actually a relationship between them. This is especially true for aerosol research where both quantities are often required together but

treated as independent quantities. This situation becomes increasingly inadequate for aerosol-related research. Our first objective is to answer the fundamental question as to whether the two quantities are related to each other, and what is the relationship. We start with pure materials, and then extend the results to mixtures such as aerosols and examine mixing rule used for calculating refractive index. A huge amount of data on pure materials (e.g., organics, inorganics and minerals) that is available in literature (most in fields other than aerosol science) are collected and examined.

2. Empirical Relationships

As two fundamental material properties, refractive index and mass density have been extensively investigated, and a wealth of data on individual quantities have been published for pure organic and inorganic compounds as well as minerals. However, in previous studies, refractive index and mass density have been treated separately and independently. To seek if there is any relationship between the refractive index and mass density, we collect, group, and examine the data sets previously published in literature for over 4000 pure organic and inorganic compounds. Figure 1 juxtaposes these results (black dots). Also shown in this figure are some data from binary mixtures (blue crosses) and from ambient aerosol particles (green triangles). Evidently, there is an overall increasing trend of refractive index with increasing mass density despite the large scatter. Furthermore, when the mass density is small such as dilute gases, the increase of refractive index with mass density is approximately linear; but the linearity gradually disappears when mass density becomes larger such as in liquids and solids.

3. Theoretical Expressions

The increase of the refractive index with increasing mass density is surprising at first glance considering the wide variety of materials involved. What is the physics underlying the positive empirical correlation between refractive index and mass density? The theoretical basis for the relationship of refractive index to mass density can be built on the polarization equations of state, i.e., the relationship

of macroscopic (bulk) material properties such as refractive index (or dielectric constant) to microscopic properties such as the molecular polarizability (Karam 1996) as follows. In this paper, all the equations are given in the “mks” unit system.

Consider a bulk material as a system of molecules that react to the incident electric field like electric dipoles. When a piece of dielectric is placed in an applied electric field, the polarization P is given by

$$P = \rho_n \alpha \epsilon_0 E_{loc}, \quad (1)$$

where ρ_n is the number density of the material, α is the mean molecular polarizability per molecule, ϵ_0 is the dielectric constant in vacuum, and E_{loc} is the mean local electric field experienced by an individual molecule. The polarization can be also related to the applied electric field E by

$$P = (\epsilon - 1) \epsilon_0 E, \quad (2)$$

where ϵ is the dielectric constant of the material. A combination of (1) and (2) yields

$$\epsilon = 1 + \alpha \rho_n \frac{E_{loc}}{E} \quad (3)$$

Elimination of E_{loc} and E using the Lorentz expression (Lorentz 1960)

$$E_{loc} = E + \frac{P}{3\epsilon_0} = \frac{1}{3}(\epsilon + 2)E \quad (4)$$

yields the so-called Clausius-Mossotti relation

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} = \frac{\alpha \rho_n}{3}, \quad (5)$$

Further application of the Maxwell relation $\epsilon = m^2$ to Eq. (5) yields the Lorentz-Lorenz expression for the refractive index (m)

$$m_s = \frac{\alpha \rho_n}{3}, \quad (6a)$$

$$m_s = \frac{(m^2 - 1)}{(m^2 + 2)}, \quad (6b)$$

where m_s is often called specific refraction. This equation has been widely used to infer molecular polarizabilities from measurements of refractive indices. In aerosol research, the mass density ρ , not the number density, is often measured and used. The two densities are simply related to each other by

$$\rho_n = \frac{N_A}{M} \rho, \quad (7)$$

where N_A is the universal Avagadro's number and M is the molecular weight of the material. After substitution of Eq. (7) to Eq. (6), the Lorentz-Lorenz expression becomes

$$m_s \equiv \frac{(m^2 - 1)}{(m^2 + 2)} = \frac{\alpha N_A}{3M} \rho. \quad (8)$$

Equation (8) is the fundamental equation that relates refractive index to mass density, and suggests a linear increase of the specific refraction with the mass density. To compare this prediction with measurements, the data shown in Fig. 1 are redisplayed in Fig. 2 in the form of the specific refraction against the mass density. Evidently, the theoretical expression describes the measurements reasonably well. This is physically understandable because, according to molecular optics, refractive index results from the collective response of electric dipoles excited by the external applied field and the number of dipoles in a given volume is closely related to the mass density (Lagendijk et al. 1997). It is noteworthy that this idea is similar to the discrete dipole approximation (DDA) for calculating light scattering by nonspherical particles (Drain and Goodman, 1993).

Equation (8) also reveals that in addition to the density, refractive index depends on the polarizability and the molecular weight as well. This dependence on the polarizability and the molecular weight of reflective index along with the large differences in these two quantities among different substances provides a physical explanation for the scatter of the data points in the above two figures.

The overall increasing trend of refractive index with increasing density suggests that the dominant role of mass density in determining refractive index.

Now we use this expression to examine the linear relationship for materials with small mass densities such as dilute gases. For such materials, there is little molecular interactions and the refractive index is close to 1. Under this condition, it can be shown by use of the Taylor expansion around $m = 1$ that Eq. (8) approximately becomes

$$m_s = \frac{(m^2 - 1)}{(m^2 + 2)} \approx \frac{2}{3}(m - 1). \quad (9)$$

Subsequently, Eq. (8) becomes

$$m = 1 + \frac{\alpha N_A}{2M} \rho \quad (10)$$

Equation indicates a linear relationship between refractive index and mass density in the limit of extreme dilutions, providing a physical explanation for the data points exhibiting a linear dependence of the refractive index on the mass density in Figs. 1 and 2. As will be shown below, Eq. (10) also has important implications for the linear mixing rule when studying inhomogeneous mixtures. Equation (8) is more general, covering gases, liquids as well as solids.

4. Effective Medium Theory

Ambient aerosol particles are generally mixtures of different chemical compositions, which leads to this theoretical question: Can and how Eq. (8) be extended to mixtures such as ambient aerosols?

One of the approaches to treating inhomogeneous mixtures is the so-called effective medium theory by which a mixture is considered a homogeneous material having effective quantities. The effective quantities of a mixture are calculated from some kind of mixing rules (Heller 1965; Ossenkopf 1991). According to Eq. (8), four quantities (mass density, molecular weight, refractive index, and polarizability) should be considered in any effective medium theory. The mixing rules for the effective

mass density and effective molecular weight are well known and straightforward from the additivities of the volume and mass. The effective density ρ_e is given by

$$\rho_e = \sum_i f_i \rho_i, \quad (11)$$

where the summation is over all the constituents of the mixture, and f_i and ρ_i are the volume fraction and the density of the i th component of the mixture, respectively. The effective molecular weight M_e is just the apparent molecular weight of a mixture given by (Wallace and Hobbs 1977)

$$\frac{1}{M_e} = \sum_i \frac{\phi_i}{M_i} = \left(\sum_i f_i \rho_i \right)^{-1} \sum_i \frac{f_i \rho_i}{M_i}, \quad (12)$$

where ϕ_i and M_i are the mass fraction and the molecular weight of the i -th constituents, respectively.

A mixing rule for the effective polarizability is necessary to complete the effective medium theory. Recall the formulation of the Lorentz-Lorenz theory on the state equation of polarization of a pure material. An implicit assumption is that every molecule of a pure substance are identical with the mean polarizability of all the molecules, i.e., the total polarizability divided by the total number of molecules. Extending this idea to a mixture, we obtain the mixing rule for the effective polarizability

$$\alpha_e = \frac{\sum_i N_i \alpha_i}{N} = \frac{\sum_i y_i N_A \alpha_i}{y N_A} = \sum_i x_i \alpha_i = \left(\sum_i \frac{f_i \rho_i}{M_i} \right)^{-1} \sum_i \frac{f_i \rho_i}{M_i} \alpha_i, \quad (13)$$

where α_e and α_i are the polarizabilities for the effective medium and the i th component of the mixture, respectively; y and y_i are the number of moles of the mixture and the i th component, respectively; x_i is mole fraction of the i th component of the mixture.

Mixing rules for calculating refractive index of a mixture have been a subject of extensive research. One of the commonly used rule is the so-called Lorentz-Lorenz mixing rule given by (Heller 1945, 1965)

$$m_{se} = \sum_i f_i m_{si} , \quad (14)$$

where m_{se} and m_{si} are the effective specific refraction and the counterpart for the i th component of the mixture, respectively. This mixing rule has been widely used in investigation of ambient aerosols (Stelson and Seinfeld 1982; Stelson 1990; Tang and Munkelwitz 1994; Tang 1996).

It is easily shown that the effective medium as defined by the above effective variables (effective molecular weight, effective density, effective polarizability and effective refractive index) satisfies the Lorentz-Lorentz equation such that

$$m_{se} = \frac{\alpha_e N_A}{3M_e} \rho_e \quad (15)$$

According to Eq. (15), just like the pure material, the effective refractive index of a mixture also increases with the effective mass density. This prediction is supported by the limited number of observational data from binary mixtures (blue crosses) and ambient aerosols (green triangles) shown in Figs. 1 and 2. Furthermore, the above set of mixing rules provides a self-consistent way to define an effective medium that involves several variables.

In aerosol research, the mass and molar concentrations are often measured as well. It is therefore desirable to formulate the effective medium equations in terms of the mass fraction ϕ_i and the mole fraction x_i in addition to the volume fraction f_i . For convenience, the three sets of equations are summarized in Table 1. It is noteworthy that the three sets of equations are equivalent and can be easily transformed to one another by use of the relation between the volume fraction f_i , the mass fraction ϕ_i and the mole fraction x_i given by

$$f_i = \frac{\rho_e}{\rho_i} \phi_i = \frac{\rho_e M_i}{\rho_i M_e} x_i \quad (16)$$

5. Implications for Mixing Rules

Besides the mixing rule given by Eq. (14), another commonly used mixing rule for calculating aerosol refractive index is the linear one, under which the effective refractive index simply is the volume-mean refractive index given by (Hanel, 1968; Ouimette and Flagan 1982; Hasan and Dzubay 1983; Lowenthal et al. 2000; Hand and Kreidenweis 2002)

$$m_e = \sum_i f_i m_i \quad (17)$$

Now the questions are: Is there a relationship between the two different mixing rules, and which one should be used in practice?

It is easy to show that this mixing rule corresponds to the linear relation between refractive index and mass density as described by Eq. (9), which holds for dilute mixtures only. In fact, this linear mixing rule is applicable to a more general class that only requires the refractive indices of every components are close to each other (we name such materials as quasi-homogeneous systems hereafter). Without loss of generality, assume all the refractive indices of a quasi-homogeneous material are close to a common value m_0 . Taylor expansion of the specific refraction around m_0 yields

$$m_s = \frac{(m^2 - 1)}{(m^2 + 2)} \approx \frac{(m_0^2 - 1)}{(m_0^2 + 2)} + \frac{6m_0}{(m_0^2 + 2)^2} (m - m_0). \quad (18)$$

Applying Eq. (18) to the specific refractive indices of the effective medium and each component of the mixture and then substituting the results into Eq. (13), we obtain the linear mixing rule given by Eq. (17).

The above derivation implies that the commonly used volume-mean rule for refractive index only works for quasi-homogeneous mixture where refractive indices of each component are similar. According to proceeding discussions, this rule quite accurately characterizes a mixture of dilute gases such as the air. However, aerosol particles normally do not exhibit this feature. Therefore, the general

Lorentz-Lorentz mixing rule should be better than the linear mixing rule in calculation of effective refractive indices of aerosol particles. Previous comparison studies also demonstrated this point (Heller 1965). These results suggest that the choice of a mixing rule for calculating effective refractive index should depend on the relationship of the refractive index to mass density. The nonlinear mixing rule as described by Eq. (18) should be used if the dependence of refractive index on mass density follows the more general Eq. (8), and the linear mixing rule should be used if the dependence of refractive index on mass density can be described by Eq. (8),

6. Concluding Remarks

Published data on refractive index and mass density for pure materials (e.g., organics, inorganics and minerals) and inhomogeneous mixtures including aerosols are collected and used to examine the relationship between refractive index and mass density. It is found that there is a general trend for refractive index to increase with increasing mass density. The Lorentz-Lorenz relation that relates dielectric constant to polarizability is introduced to quantify the relationship between refractive index and mass density for pure materials, providing a physical explanation for this positive correlation. The formulation is further extended to inhomogeneous mixtures such as aerosols by establishing a self-consistent effective medium theory. The commonly used mixing rules for calculating effective refractive index are derived from the effective medium theory and compared in view of the corresponding relationship between refractive index and mass density. The result indicates that not only refractive index and mass density are related to each other, but also this relationship is pivotal for choosing the appropriate mixing rule for calculating effective refractive index of aerosol particles.

Several points are noteworthy. First, the data on the effective refractive index and mass density used in this paper are limited; more data are needed to substantiate the finding. Second, there has been some confusion on the mixing rules used in calculation of effective refractive index and mass density.

This issue deserves some attention in future research. Finally, a single value is often assigned to aerosol particles regardless of their sizes. However, many studies have shown that some aerosol particles such as combustion aggregates often assume open, fractal-like structures with mass density depending on particle sizes (Sorensen 2001). Mass densities of solid hydrometeors (e.g., snowflakes, graupels and hailstones) are also found to depend on particle sizes (Pruppacher and Klett 1997). The relationship of refractive index to the mass density suggests that the effective refractive index should be size-dependent for these particles as well.

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Figure Captions

Figure 1. Dependence of refractive index on mass density. The black dots are data for pure materials, including organic compounds, inorganic compounds and minerals from on line handbooks (www.knovel.com). Blue dots are for binary mixtures such as salt solutions. The green triangles represent a few data points for ambient aerosol particles.

Figure 2. Same as Fig. 1, except for the specific refractive index on mass density.

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Table 1. Self-Consistent Mixing Rules for Effective Inhomogeneous Mixtures

Effective variables	Volume fraction f_i	Mass fraction ϕ_i	Mole fraction x_i
Molecular weight	$\frac{1}{M_e} = \frac{1}{\rho_e} \sum_{i=1}^N \frac{\rho_i f_i}{M_i}$	$\frac{1}{M_e} = \sum_{i=1}^N \frac{\phi_i}{M_i}$	$M_e = \sum_{i=1}^N x_i M_i$
Density	$\rho_e = \sum_{i=1}^N f_i \rho_i$	$\frac{1}{\rho_e} = \sum_{i=1}^N \frac{\phi_i}{\rho_i}$	$\frac{1}{\rho_e} = \frac{1}{M_e} \sum_{i=1}^N \frac{M_i x_i}{\rho_i}$
Polarizability	$\alpha_e = \left(\frac{f_i \rho_i \alpha_i}{M_i} \right)^{-1} \sum_{i=1}^N \frac{f_i \rho_i \alpha_i}{M_i}$	$\alpha_e = \left(\sum_{i=1}^N \frac{\phi_i}{M_i} \right)^{-1} \sum_{i=1}^N \frac{\phi_i \alpha_i}{M_i}$	$\alpha_e = \sum_{i=1}^N x_i \alpha_i$
Specific refraction	$m_{se} = \sum_{i=1}^N f_i m_{si}$	$m_{se} = \left(\sum_{i=1}^N \frac{\phi_i}{\rho_i} \right)^{-1} \sum_{i=1}^N \frac{\phi_i}{\rho_i} m_{si}$	$m_{se} = \left(\sum_{i=1}^N \frac{x_i M_i}{\rho_i} \right)^{-1} \sum_{i=1}^N \frac{x_i M_i}{\rho_i} m_{si}$
Molar refraction	$R_e = \frac{M_e}{\rho_e} \sum_{i=1}^N \frac{f_i \rho_i}{M_i} R_i$	$R_e = M_e \sum_{i=1}^N \frac{\phi_i}{M_i} R_i$	$R_e = \sum_{i=1}^N x_i R_i$

$R = m_s \frac{M}{\rho} = P_R = \frac{N\alpha}{3}$, where P_R is referred to as molar polarization. Molar polarization is the molar fraction for zero frequency. Mole fraction = ratio of the number of moles of one constituent of a mixture or solution to the total number of moles of all the constituents.

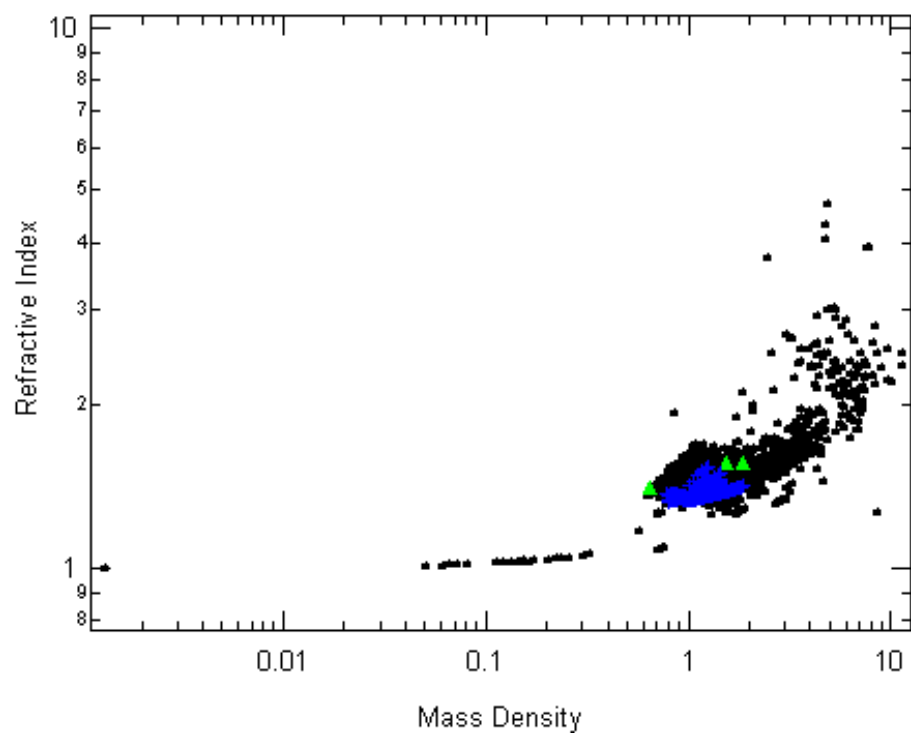


Fig.1

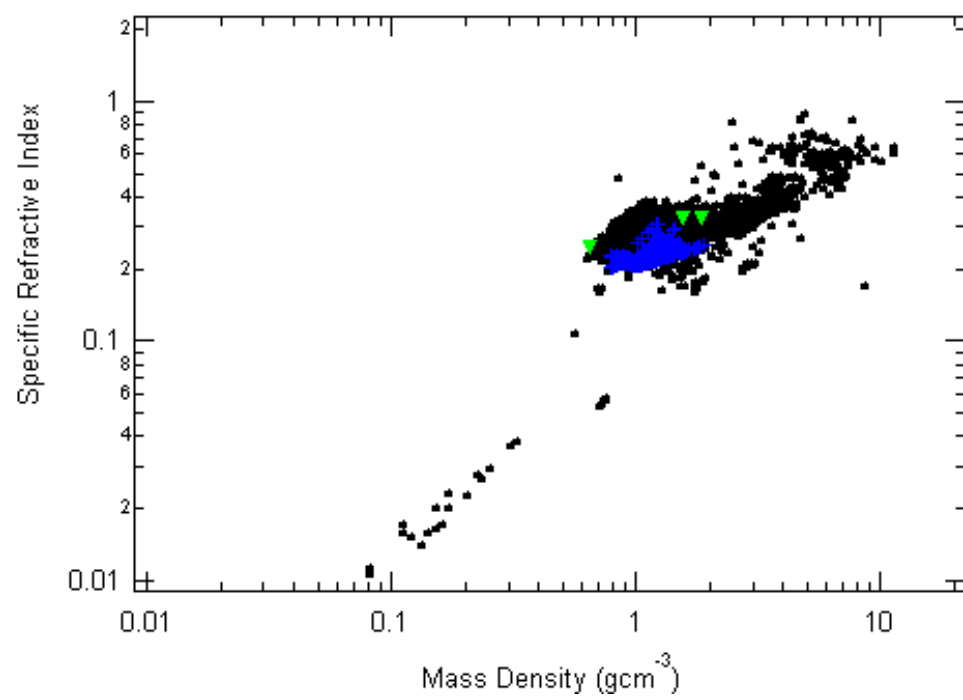


Fig. 2.